DYNAMICS OF SUPERCOOLED BINARY LIQUIDS

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In this paper we investigate the relaxation of density fluctuations in a disparate-size binary liquid mixture near the glass transition. We apply the mode-coupling theory of the glass transition to a two-component system focussing our attention on the difference in dynamical behavior of big and small particles. We compare our results with predictions of the one-component theory[1].

Mode-coupling theory[2] is summarized in the following 2×2 -matrix equation-of-motion governing space- and time-variations of the partial density-relaxation functions, $\Phi_{ss'}(q,t) \propto \sum_{i,j} < \exp\left\{-i\mathbf{q}\cdot\left[\mathbf{r}_j^{(s)}(t) - \mathbf{r}_i^{(s')}(0)\right]\right\} >$ with $s, s' = 1, 2$ denoting the particle species and $q > 0$ a wavenumber:

$$\ddot{\Phi}(q,t) \; + \; \Omega^2(q)\cdot\Phi(q,t) \; + \; \int_0^t dt'\; K(q,t-t')\cdot\dot{\Phi}(q,t') \; = \; 0\,, \tag{1}$$

$$\begin{aligned} K_{ss'}(q,t) \; = \; & \frac{v_s^2}{n_{s'}V}\sum_{ll'}\sum_{\mathbf{k}} k_z u_{ls}(k)\Big[\; k_z u_{l's'}(k)\Phi_{ll'}(k,t)\Phi_{ss'}(\kappa,t) \\ & + \kappa_z u_{l's'}(\kappa)\Phi_{ls'}(k,t)\Phi_{sl'}(\kappa,t)\;\Big] \; + \; \Gamma_{ss'}(q)2\delta(t) \end{aligned} \tag{2}$$

with abbreviations $n_s = N_s/V$, $v_s^2 = k_BT/m_s$, $k_z = \mathbf{k}\cdot\mathbf{q}/q$, and $\kappa = \mathbf{q} - \mathbf{k}$. Here $\Omega^2_{ss'}(q) = q^2\, v_s^2\sqrt{n_s/n_{s'}}\,[S(q)^{-1}]_{ss'}$ and $u_{ss'}(q) = -k_BT\left\{\delta_{ss'} - [S(q)^{-1}]_{ss'}\right\}$ are determined by the static structure factors $S_{ss'}(q)$. While the quickly decaying last term in Eq.(2) describes binary-collision effects, the $\mathbf{k}$-integral approximates multiple-collision processes of the dense liquid causing strong dynamical feedback. This feedback is monitored by the relaxation functions appearing in the integrand of Eq.(2). Implementing initial conditions $\Phi_{ss'}(q,0) = S_{ss'}(q)/(k_BT)$ and $\dot{\Phi}_{ss'}(q,0) = 0$ the set of nonlinear equations (1) – (2) can be solved by iteration.

We applied the theory to a binary hard-sphere mixture characterized by three parameters: the total packing fraction $\eta = n_2\sigma_2^3[1 + c_1\delta^3/(1-c_1)]\pi/6$, the size ratio $\delta = \sigma_1/\sigma_2$, and the concentration of small particles $c_1 = N_1/(N_1+N_2)$. For $\delta = 0.2$ and $c_1 = 0.5$, we solved the coupled equations (1) – (2) numerically for various η with $S(q)$ as input determined from the solution of the Percus-Yevick equation for the binary hard-sphere mixture[3]. In our previous paper[2], we analyzed single-particle properties such as localization lengths and diffusion constants. Also we found *two* transition points: Increasing the packing fraction η starting from the liquid side, the big particles make a glass at $\eta_B = 0.52$, while the small particles retain a finite mobility. The diffusion constant of the small particles becomes zero at $\eta_A = 0.53$. (Note that the transition at $\eta = \eta_A$ is of Type-A and the one at $\eta = \eta_B$ is of Type-B[1].) In the following, we extend the analysis to examine the *coherent* density-relaxation functions of the big and small particles.

Figure 1 shows the susceptibility $\chi''_{ss}(q,\omega) = \omega\int_0^\infty e^{it\omega}\Phi_{ss}(q,t)k_BT/S_{ss}(q)$ for various η in the liquid phase. In $\chi''_{22}(q,\omega)$ a large α-peak is observed in the low-frequency regime, and a microscopic peak appears at $\omega/\omega_0 \sim 10$, which is overdamped in the present model. Near the transition point η_B, a small β-peak can be observed at $\omega/\omega_0 \sim 10^{-2}$, which merges with the high-frequency wing of the α-peak as η is decreased. These features of $\chi''_{22}(q,\omega)$ are the same as those found for a one-component liquid. The relaxation of the big particle's density fluctuations is similar to that of a one-component system. For the small particles, on the other hand, we find a large peak at $10^{-1} < \omega/\omega_0 < 1$ with a shoulder at high frequencies. This high-frequency shoulder is a remainder of the microscopic peak. The large peak in $\chi''_{11}(q,\omega)$, the intensity of which is much higher than that of the α-peak, is expected to arise from the β-relaxation of the small particles.

Our interpretation of the results is the following. As reported in our previous paper[2], the diffusion constant of the small particles near the transition is about 10^5 times larger than that of the large particles. Therefore, on the time-scale of the small particles, the large particles are almost frozen and produce a random potential which the small particles will experience when moving through the matrix. The large peak found in $\chi''_{11}(q,\omega)$ is considered to arise from the relaxation of the small particles *within* the random potential, while the α-peak in $\chi''_{22}(q,\omega)$ reflects the decay *of* the random potential. In our disparate-size mixture the two types of decay process are clearly separated. As a result, the characteristics of $\chi''_{11}(q,\omega)$ are quite different from those of a one-component system, while the behavior of the large particles is almost the same as that in a one-component liquid. These results point out the necessity of treating a multi-component theory when dealing with multi-component systems.

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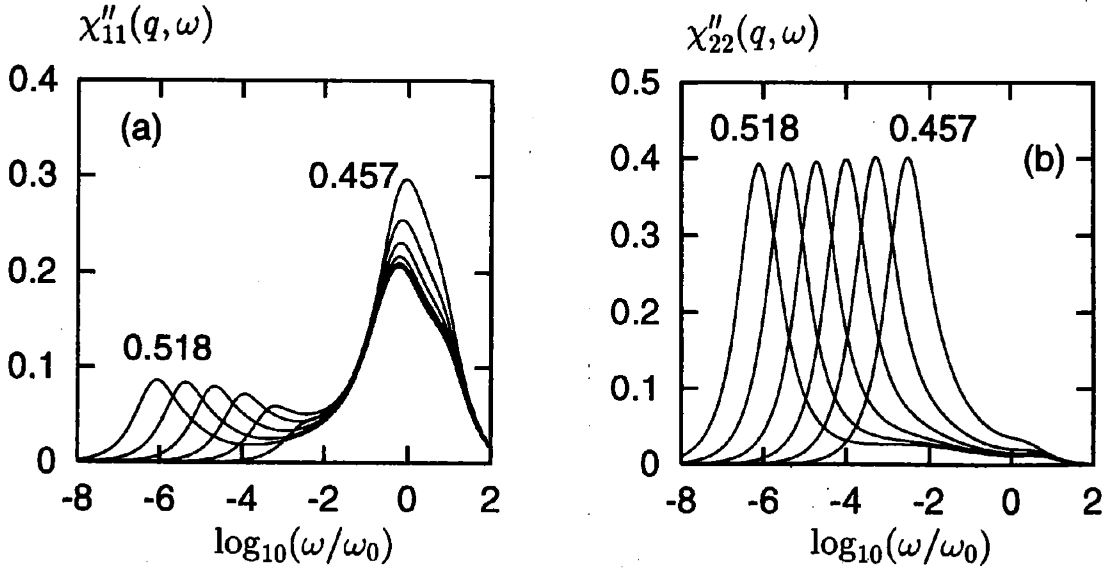

Fig.1 Generalized susceptibility $\chi''_{ss}(q,\omega)$ for (a) small particles (s=1) and (b) big particles (s=2), where $\eta = \eta_B - (1/2)^n$, $n = 4 \sim 9$.

References

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